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^{1}H and ^{31}P nuclear magnetic resonance study of proton-irradiated KH_2PO_4

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We have studied the microscopic structure and dynamics in a proton-irradiated KH_2PO_4 single crystal. Our ^{1}H and ^{31}P nuclear magnetic resonance measurements indicate that proton irradiation gives rise to a decrease in the local dipolar order of the rigid lattice protons and an increase in interstitial protons as well as structural distortion of the PO_4 tetrahedra.

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In the well-known structural phase transition of KH_2PO_4 (KDP) at $T_c = 122$ K involving ferroelectricity,[1] it is known that protons in the double well potentials in the hydrogen bonds are involved, accompanied by displacements in the heavy atom (K, P, and O) structure. One outstanding phenomenon is the proton-deuteron "isotope effect" that raises the transition temperature by about 100 K and decreases the pressure dependence of the transition temperature. Traditionally, the proton-deuteron isotope effect has been explained by the tunneling model, in which the marked increase in the transition temperature was attributed to a change in the tunneling frequency by the mass change, and the decrease in the transition temperature with increasing pressure was attributed to an increase in the tunneling integral.[2] Nelmes *et al.* have shown the isotope effect to be due only slightly to the deuteron mass affecting the tunneling probability, and much more to the change in the O-O separation.[3] According to recent neutron Compton scattering experiments, the protons are self-trapped in one or the other of their equivalent positions, and jump from position to position through phonon-assisted tunneling.[4] Reiter *et al.* have also proposed that the proton is coherent over both sites, implying tunneling.[5] The tunneling model has mainly been concerned with the proton-deuteron mass difference and does not take into account the effect of the hydrogen bond geometry. While Sugimoto and Ikeda have proposed a model in which the H-D isotope substitution induces PO_4 tetrahedral distortion, giving rise to a change in the ground state energy, increasing the phase transition temperature,[6] the model has yet to be experimentally tested.[6,7] In this regard, here we show that proton irradiation opens an alternative opportunity of studying the effects of the microscopic structural modification of the hydrogen bond geometry and PO_4 tetrahedral distortion in the KDP-type ferroelectrics.

The geometrical aspects of the hydrogen bonds were considered in the proton-lattice coupling model,[8,9] and redistribution of the atomic positions by the electric-field-induced structural changes was suggested.[10,11] In recent publications,[12,13] we have shown the effects of proton irradiation on the structure and dielectric constant of the KDP-type crystals. It is the purpose of this work to further elucidate the microscopic changes induced in a KDP single crystal by proton irradiation by means of ^{1}H and ^{31}P NMR.

A KDP single crystal was supplied by the Crystal Bank at Pusan National University, and was irradiated with 1 MeV protons to a dose of 10^{15} ions/cm^2. A Bruker MSL 200 spectrometer was used for ^{1}H NMR measurements at the frequency $\omega_o/2\pi = 200$ MHz. The ^{1}H NMR line shapes were obtained by Fourier transforming the free-induction decay signals. A Bruker DSX 400 spectrometer was used for ^{31}P NMR measurements at the frequency $\omega_o/2\pi = 161$ MHz, the chemical shift being measured relative to a ^{31}P standard, an 85% aqueous solution of H_3PO_4.

The ^{1}H NMR line shape was well fitted by a Pake doublet with Gaussian dipolar broadening, representing rigid lattice protons, and a Lorentzian component, representing mobile interstitial protons (inset of Fig. 1). The dipolar splitting arises from the rigid lattice protons, and the Pake doublet arises from the proton configuration around the PO_4 tetrahedra, reflecting the two-spin proton dipolar interaction obeying Slater's ice rule.[14] Figure 1 shows a marked decrease in the dipolar splitting of the Pake doublet of the KDP samples, reflecting local dipolar order, after the proton irradiation.

Figure 2 shows the temperature dependence of the ^{1}H NMR linewidth of the Lorentzian component before and after the proton irradiation. The increased linewidth after the irradiation is indicative of decreased mobility for the mobile protons, presumably undergoing interbond hopping motions,

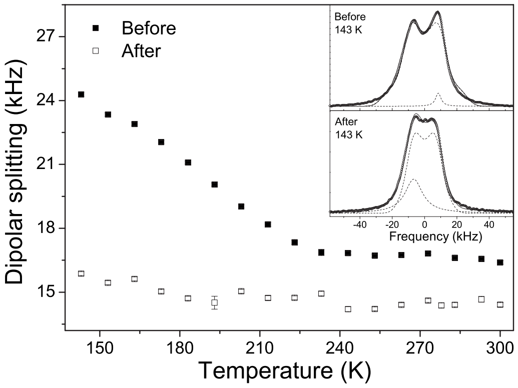

FIG. 1. Temperature dependence of the dipolar splitting of the ^{1}H NMR line shape of the KDP single crystal before and after the irradiation. Inset: ^{1}H NMR line shapes at 143 K before and after the proton irradiation, fitted by a dipolar-broadened Pake doublet and a Lorentzian component.

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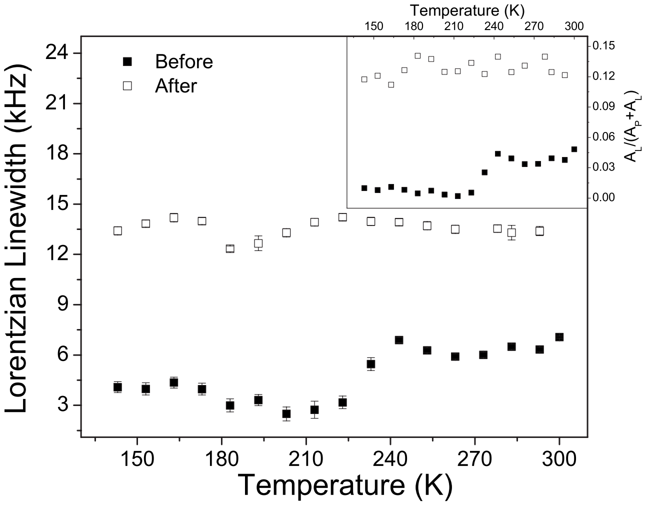

FIG. 2. Temperature dependence of the ^{1}H NMR linewidth of the Lorentzian line component in KDP before and after the irradiation. Inset: Intensity fraction of the Lorentzian line component before and after the proton irradiation.

whereas the increased intensity fraction of the Lorentzian line shape (inset of Fig. 2) indicates increased population of the interstitial mobile protons after the irradiation. The interstitial protons, undergoing interbond hopping motions, are attributed to the defects in the hydrogen bond. The increase of the interstitial protons in Fig. 2 may be ascribed to increased hydrogen bond defects as the interstitials implanted by the proton irradiation can account for only a tiny portion of the total population.[13]

It is worthwhile to compare the behavior of the mobile interstitial protons observed in this work with the ^{1}H NMR second moment measurements reported in our previous work.[13] It is to be noted that while the second moment that is dictated by the "rigid lattice" protons accounting for most of the NMR intensity indicates motional narrowing, in agreement with the decrease in the activation energy indicating higher proton mobility, the slowed proton mobility indicated in Fig. 2 corresponds to the Lorentzian line component of the line shape arising from the mobile interstitial protons. Thus, it is interesting that proton irradiation gives rise to contrasting effects to the motions of the rigid lattice protons participating in the hydrogen bond and the interstitial protons not participating in the hydrogen bond.

In order to further identify the effect of the proton-beam irradiation on the local environment of the KDP crystal, the angular rotation patterns of ^{31}P NMR were obtained as shown in Fig. 3. In the paraelectric phase, the ^{31}P nuclei sit at the centers of the PO_4 tetrahedra which are linked by the O-H$\cdots$O hydrogen bonds to form a three-dimensional lattice. At $T=296$ K$>T_c$, all the phosphorus sites were found to be chemically and physically equivalent.[15] After the irradiation, the principal chemical shift tensor components σ_{11} and σ_{22} decreased to 40% of those before the irradiation, and the anisotropy, $\Delta\sigma=\sigma_{\parallel}-\sigma_{\perp}$, was -29.25 and -26.48 ppm before and after the proton-beam irradiation, respectively (Table I). The ^{31}P chemical shift tensor in the principal axes $(\sigma_{\perp})$ is a sensitive indicator of the hydrogen bond directions; the ^{31}P anisotropic chemical shift tensor exhibits a significant change along the crystallographical *a* and *b* axes in the hydrogen bond directions after the proton-beam irradiation. Our ^{31}P NMR anisotropic chemical shift tensor measurements, thus, indicate that the proton-beam irradiation treatment can, in fact, modify the lattice configuration along the hydrogen bond directions, and the local structure with the distortion of the PO_4 tetrahedra consequently gives rise to charge redistribution.

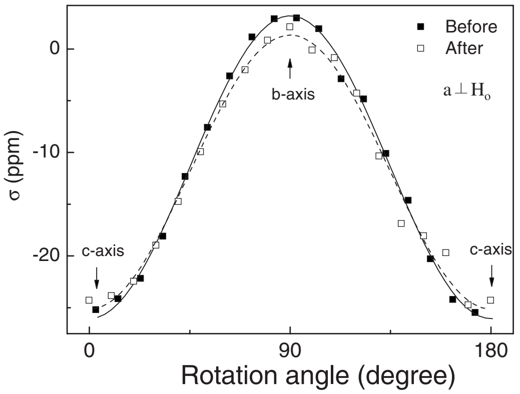

FIG. 3. Angular dependence of the ^{31}P chemical shift before and after irradiation in a single crystal of KH_2PO_4 at $T=296$ K.

The chemically shifted resonance frequency ω depends on the local field of the crystal with respect to the resonance frequency ω_o without chemical shift, according to $\omega=\omega_o(1-\sigma)$, with the chemical shielding tensors depending on the electronic charge distribution. The decrease of the chemical shift in the hydrogen bond direction after the irradiation corresponds to up-field, paramagnetic shielding, indicating increased electron density on the nearby P-O bonds lying in the hydrogen bond direction. The most up-field component of the shielding tensor turns out to lie along the P-O direction, which is the direction of highest electron density,[16] in good agreement with our previous results.[13]

In summary, we have studied the effect of the proton-beam irradiation on a single crystal of KH_2PO_4, which is a typical hydrogen-bonded ferroelectric system. As a result, a decrease in the local dipolar order after the proton irradiation was revealed by the ^{1}H NMR line shape measurements, as well as an increase of mobile interstitial protons with slowed motions. Besides, structural distortion of the PO_4 tetrahedra was revealed by our ^{31}P NMR chemical shift measurements.

TABLE I. ^{31}P NMR chemical shift tensors before and after the irradiation for KH_2PO_4 (in ppm).

Before $\sigma=\begin{pmatrix}3.20 & 0 & 0\\ 0 & 3.20 & 0\\ 0 & 0 & -26.05\end{pmatrix}$,	$\Delta\sigma=\sigma_{\parallel}-\sigma_{\perp}=-29.25$
After $\sigma=\begin{pmatrix}1.35 & 0 & 0\\ 0 & 1.35 & 0\\ 0 & 0 & -25.13\end{pmatrix}$,	$\Delta\sigma=\sigma_{\parallel}-\sigma_{\perp}=-26.48$

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